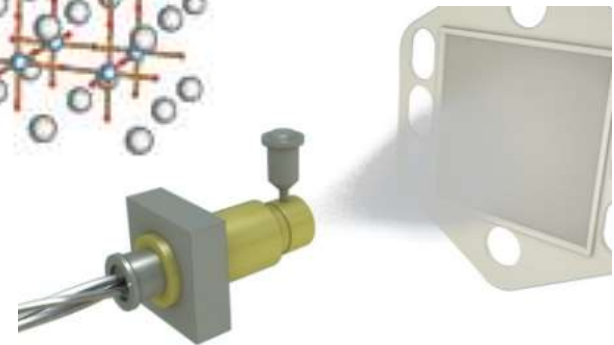
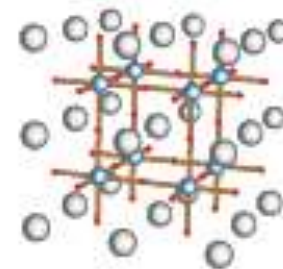




Development of a Thermal Spray, Redox Stable, Ceramic Anode for Metal Supported SOFC

Richard Hart
GE Global Research
Kick-Off Dec 2, 2015



Imagination at work.

SOFC Innovative Concepts and Core Technology Research
DE-FOA-0001229 Award FE0026169

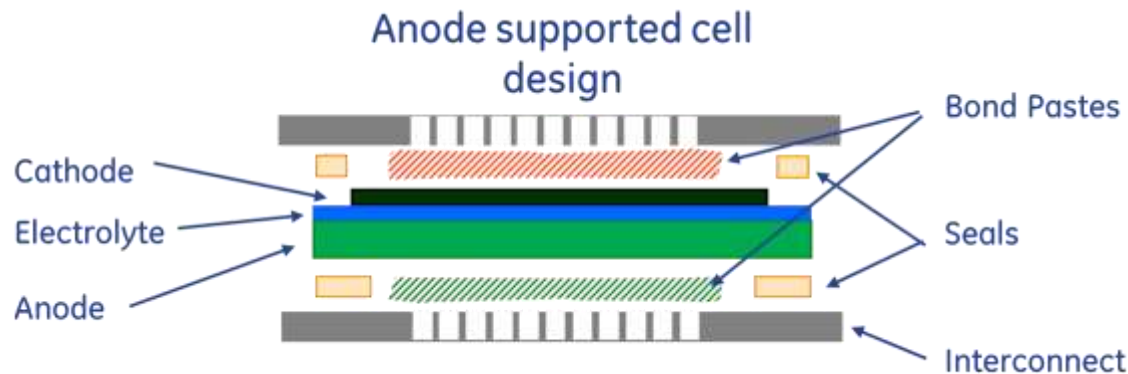
 Trademark of General Electric Company

Outline:

- Background (3-10)
- Project Objective (11)
- Team Structure(12)
- Project Overview & Budget (13)
- Risk Assessment Overview (14)
- Detailed Project Plan, PMP/SOPO (15-24)
- Acknowledgments (25)

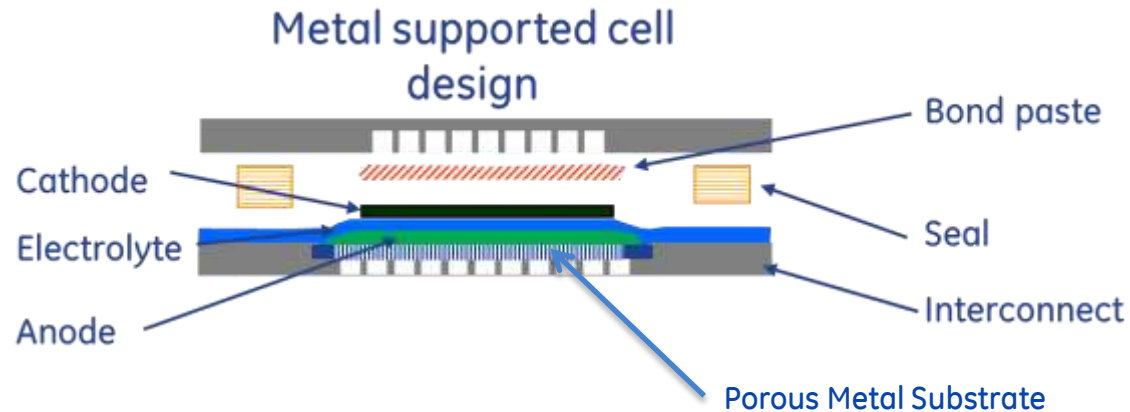


Metal supported cells



Advantages:

- Integrated anode seal
- Electrolyte in compression
- Improved anode electrical contact
- Increased active area
- Lower anode polarization

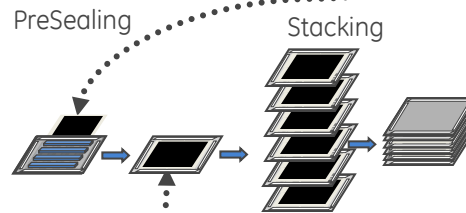
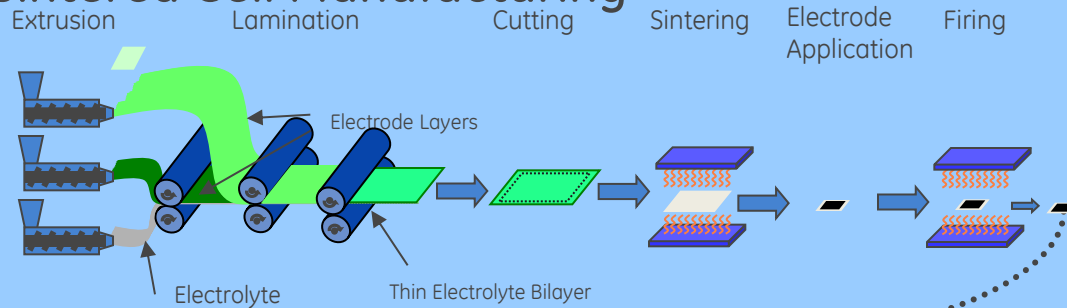


Challenges:

- Dense / hermetic electrolyte
- Porous metal substrate degradation

Low-cost manufacturing

Sintered Cell Manufacturing



Advantages

Larger area / Scalable
Simplified sealing
Low Capex / Modular
Lean Manufacturing

Thermal Spray



Leverage GE thermal
spray expertise

Proposed GE Product: Distributed Energy

- Electric output: 1-10MW
- 60- 65% efficiency
- NG Fueled
- Minimal site installation
- Turn down capability
- Low GHG emissions



GE's new "Internal Start Up"



- Fastworks approach drives speed to market and customer value
- Internal incubation with independent leadership
- Ramping up off site facility with pilot manufacturing capability

Speed, agility and focus of a small start-up ...
with access to all the strength of a big company



Fuel Cell Pilot Facility – Malta NY



Traditional NiO(Ni)/YSZ anodes

- Advantages:

- High initial electrochemical activity
- Good electronic conductivity
- Low cost
- Well understood, wealth of data

- Disadvantages:

- High redox Vol change (fuel \leftrightarrow air)
- Ni particle ripening/poisoning
- EHS concerns (NiO)
- Sourcing concerns (REACH in Eu)



Anode Redox Stability → What is it? Why do we care?

- Redox Cycling is when the environment on an SOFC electrode changes from reducing \leftrightarrow oxidizing at high temperatures (where chemical changes can happen).
- Ni/YSZ anodes undergo volume changes during these kind of events.
- Even if the system provides back up for loss of fuel condition:
 - During system/stack startup, all electrodes produced w/ NiO reduce to Ni imparting stress.
 - Minor perimeter seal leaks can lead to localized re-oxidation of $\text{Ni} \rightarrow \text{NiO}$. This can lead to localized stress & cracking.



Combining thermal spray & ceramic anodes

- *Thermal spray manufacturing avoids the challenges of “co-sintering” of anode w/ electrolyte*
 - Sintering stresses/warpage, side reactions, solid solutions
- Possibly widens anode material exploration set to materials w/ poor sinterability
- Scalable deposition process minimizes material use, allows for easy scale up to large foot-print cells
- Thermal spray makes gradient microstructures/chemistries and tailored microstructures possible



Project Objective

Program Team



GE Global Research

- Thermal spray coatings
- SOFC fundamentals
- Material degradation
- Powder agglomerate engineering



GE Fuel Cells

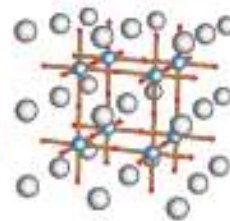
- Cell & stack design
- Thermal spray scale up
- Systems design & engineering

West Virginia University

- Ceramic anode chem dev.
- Material physics/property analysis
- Nano-ceramic synthesis

Program Objective: Combine GE thermal spray SOFC manufacturing technology with redox stable ceramic anode materials to produce robust, redox tolerant, SOFC large scale cells. Program begins with the development of thermally sprayed electrode compositions and layers, and culminates in the scale up and test of a 5kW stack on natural gas fuel.

Development of Redox Stable Anode Material Compatible with Thermal Spray



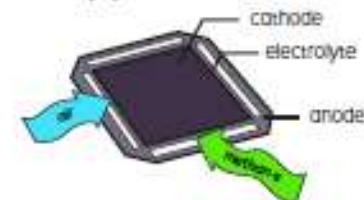
Powder Engineering, Microstructure Control



Flexible Thermal Spray Processing System



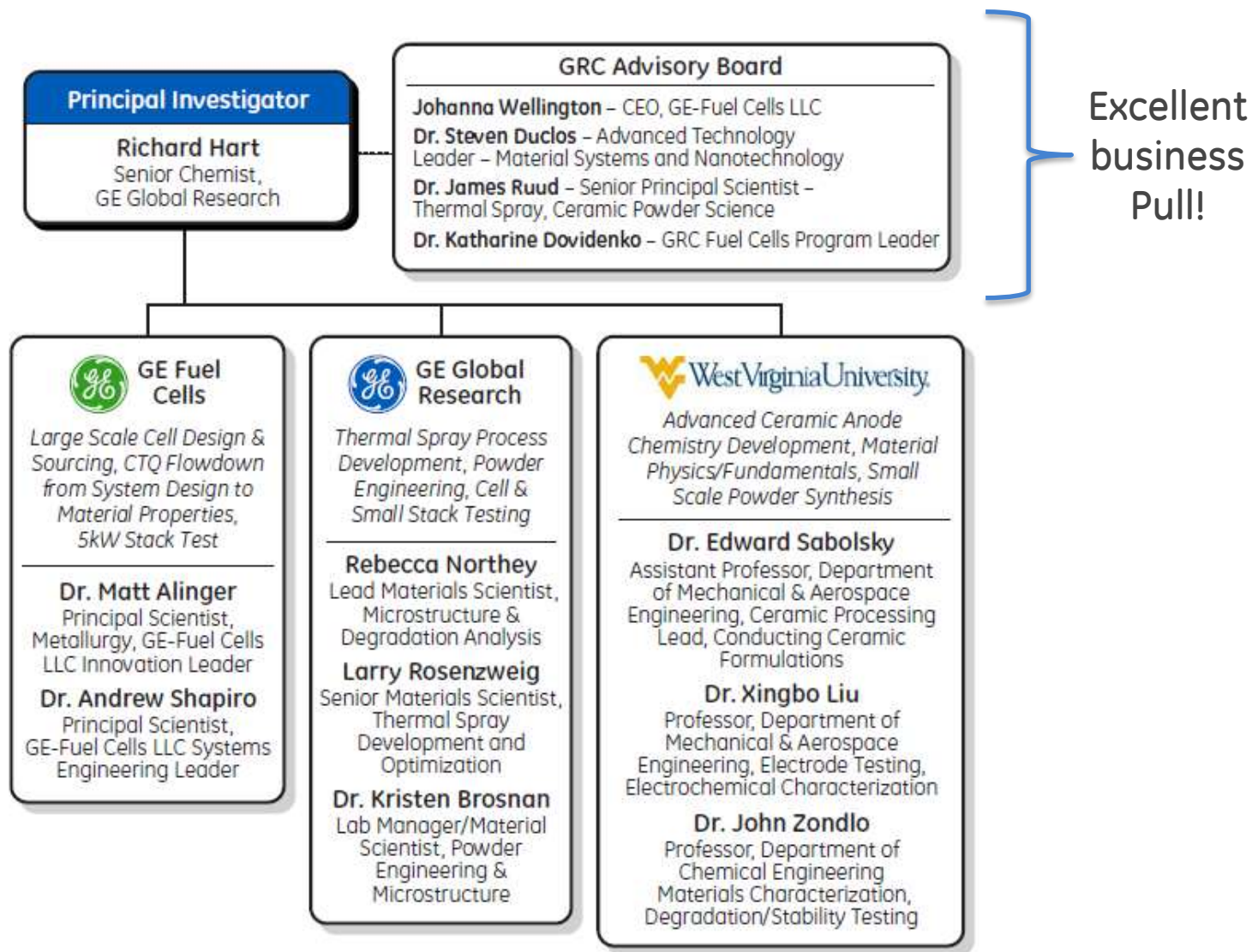
400 cm² Metal-Supported SOFC Cell



- High fuel utilization/power density
- Thermal cycle tolerant
- Scalable to large sizes



Team Structure



Project Overview & Budget

Task	Owner	Timing	Objectives
1	GE Global Research	Months 1-36	<ul style="list-style-type: none"> Defined by DOE; risk management, coordination, reporting
2	GE Global Research GE-Fuel Cells	Months 1-12	<ul style="list-style-type: none"> Derive anode layer requirements from existing systems models Tailor Global Research thermal spray process using single baseline composition Streamline (cost and lead time) powder engineering methods Establish redox cycle cell test procedures
3	West Virginia University	Months 1-24	<ul style="list-style-type: none"> Develop key materials properties measurements Hand off to GRC SET1 and SET2 Anode Compositions
4	GE Global Research	Months 13-27	<ul style="list-style-type: none"> Optimize thermal spray process for improved formulations Go/No – Does single scaled cell (100-400cm²) meet CTQs?
5	GE Global Research GE-Fuel Cells	Months 28-36	<ul style="list-style-type: none"> Powder scale up, cell fabrication scale up. Build and test, 5 kW SOFC stack for 1000 hr, Nat Gas/Sim Nat Gas fuel.

DOE \$ Costing Profile:

Team Member	Total
GE Global Research	2,150,956
University of West Virginia	497,268
Total	2,648,224

Our project will likely be underspent in 2015,
Relative to our original linear spend plan,
Due to ramping-up of resources on the project.

We will increase our effort in 2016 to
Correct the course and prevent deliverable
Slip.

25% GE+WVU cost share



Risk Assessment

1st Risk assessment from March 2015 was updated Oct 2015, shortly after Receiving funding.

We identified 16 key risks: 3 high, 10 medium, 3 low

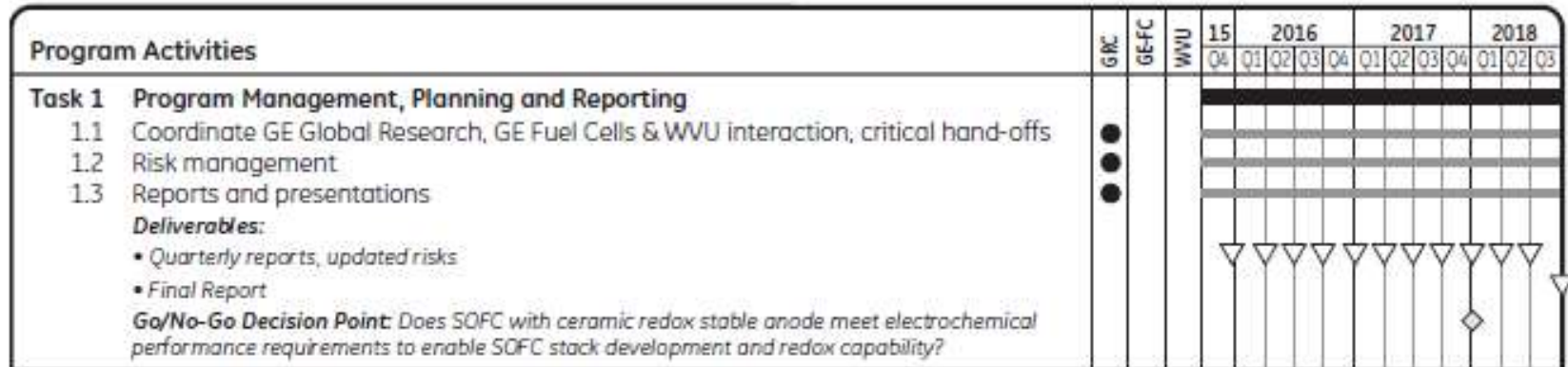
GE's Fastworks/Six Sigma mindset -> project plan geared to address the highest impact risks first:

Key Risk Area/Type	Task #s	Abatement Strategy
H - Lower power density from new ceramic anodes (or degradation)	Task 2&4 Task 3	GRC, optimize spray parameters & powder morphology to increase surface area WVU, develop new higher performing formulations
H -Scale up issues due to a narrow operational window	Task 2	Power homogenization, collect agglomerate characterization data, map thermal spray processing window & use Six Sigma
H - Pilot scale agglomeration is pricey and long lead	Task 2	Early engagement with vendors (started ~June 2015), identify pilot scale spray drying with acceptable \$ and lead time
M - Electrode stability Issues (phase or chemistry instability, resistive phase formation, interaction w/ metal or YSZ)	Task 2	XRD analysis of coupons, compositional analysis (ICP/XRF), Thermal spray optimization, SEM analysis of electrodes and electrode interfaces, cell testing

As with all projects, we expect new risks to arise, team will update Risk Assessment quarterly.



Detailed Project Plan – Task 1 (all 3 years)



- Richard Hart @ GE is primarily responsible for Task 1
- Focus: communication (includes GE↔WVU hand-offs), reporting, risk management
- Will use GE's Six Sigma/Fastworks methodology. Focus on the right problems -> identify and retire key risks.



Task 2 – GE Global Research (Year 1)

Program Activities	GRC	GE-FC	WVU	15	2016				2017				2018		
				04	01	02	03	04	01	02	03	04	01	02	03
Task 2 Preliminary Assessment of Thermal Spray Ceramic Redox Stable Anodes															
2.1 Develop system level approach/model to determine catalytic/electronic property requirements of ceramic redox stable anode for solid oxide fuel cell integration	●	●													
2.2 Define and measure key material and electrochemical properties of Ni/YSZ and baseline LST and LST/doped CeO ₂ anode powders	●														
2.3 Develop baseline LST/CeO ₂ anode thermal spray powders and optimize spray conditions for anode deposition	●														
2.4 Evaluate performance and degradation of baseline LST and LST/CeO ₂ redox stable anodes on metal supported cell architecture	●														
Deliverables:															
• Summary of catalytic and electronic anode requirements for SOFC system															
• Initial performance of baseline LST/CeO ₂ redox stable anode on metal supported cell architecture and sensitivity to key materials properties															
Milestones:															
• Demonstration of thermal sprayed LST/CeO ₂ based anode layer															
• Demonstration of improved redox performance of ceramic anode based cell															

Task 2.1 – Specification definition (“mini”QFD finished, modeling started)

Task 2.2 – Long lead items ordered, measurement system analysis underway

Task 2.3 – 1st agglomerated powder arrived 11/18, thermal spray trials expected to start Dec-Jan.

Task 2 goal → “Make it Work”



Task 2 - Why start with LST/dCeO₂?



- good e- cond
- redox stable
- low pricing
- good CTE match

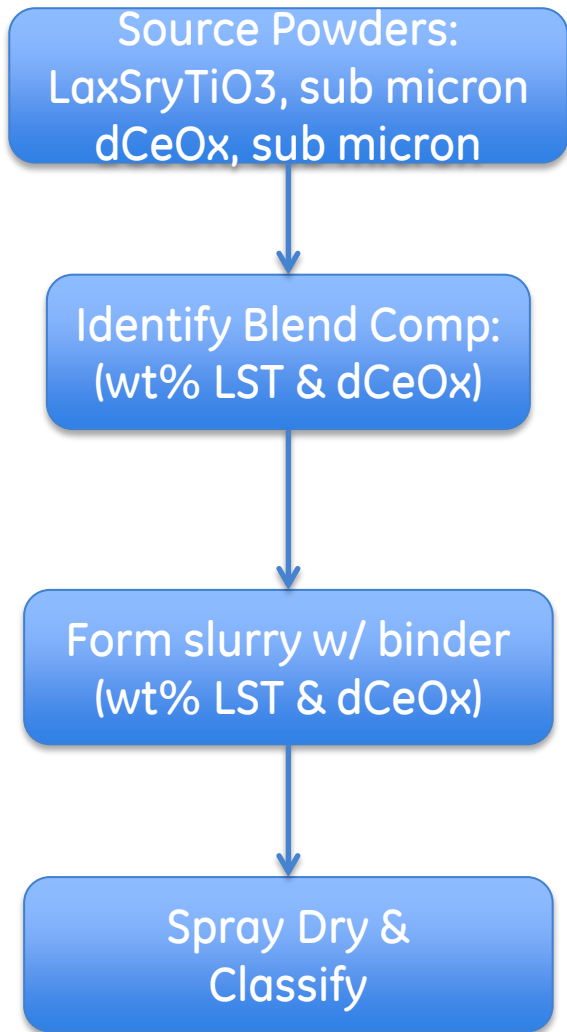


- excellent ion conductivity
- good catalytic properties
- MEIC (enhances TPB)

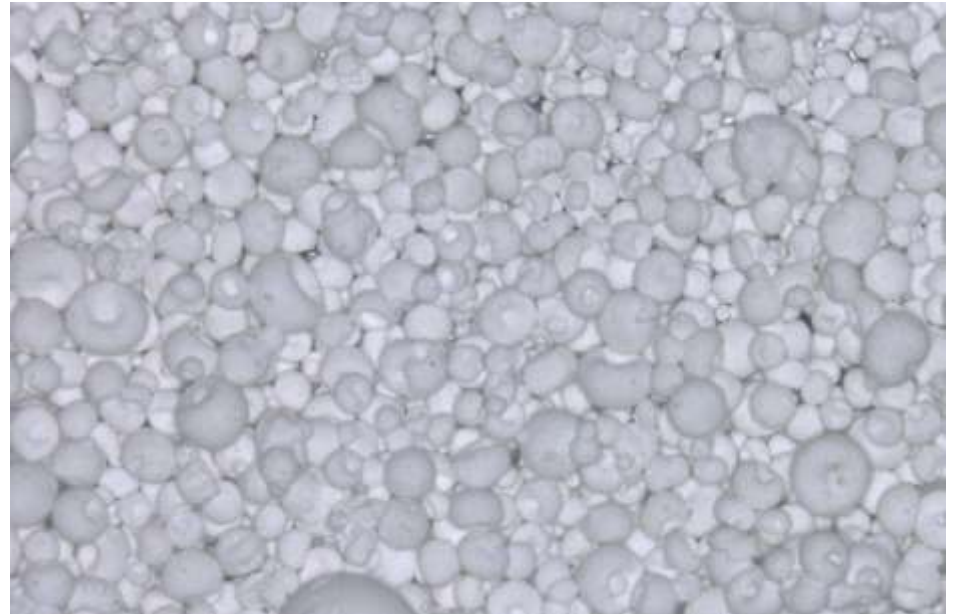
- Known system w/ potential to meet most of the anode layer requirements. Previously well studied using sintering fab.
- Platform for GE to develop: powder feedstock vendors, microstructure control, understand perf. relationships to key mat properties, elucidate unknown risks



Task 2 - Spray Agglomeration Processing



Example product agglomerated undoped SrTiO3



Ideal Product:

- Easily flowable powder (inject into plasma)
- Controlled & Repeatable PSD
(important for process scaling & reproducibility)



Task 2 – Thermal Spray Work Flow Diagram

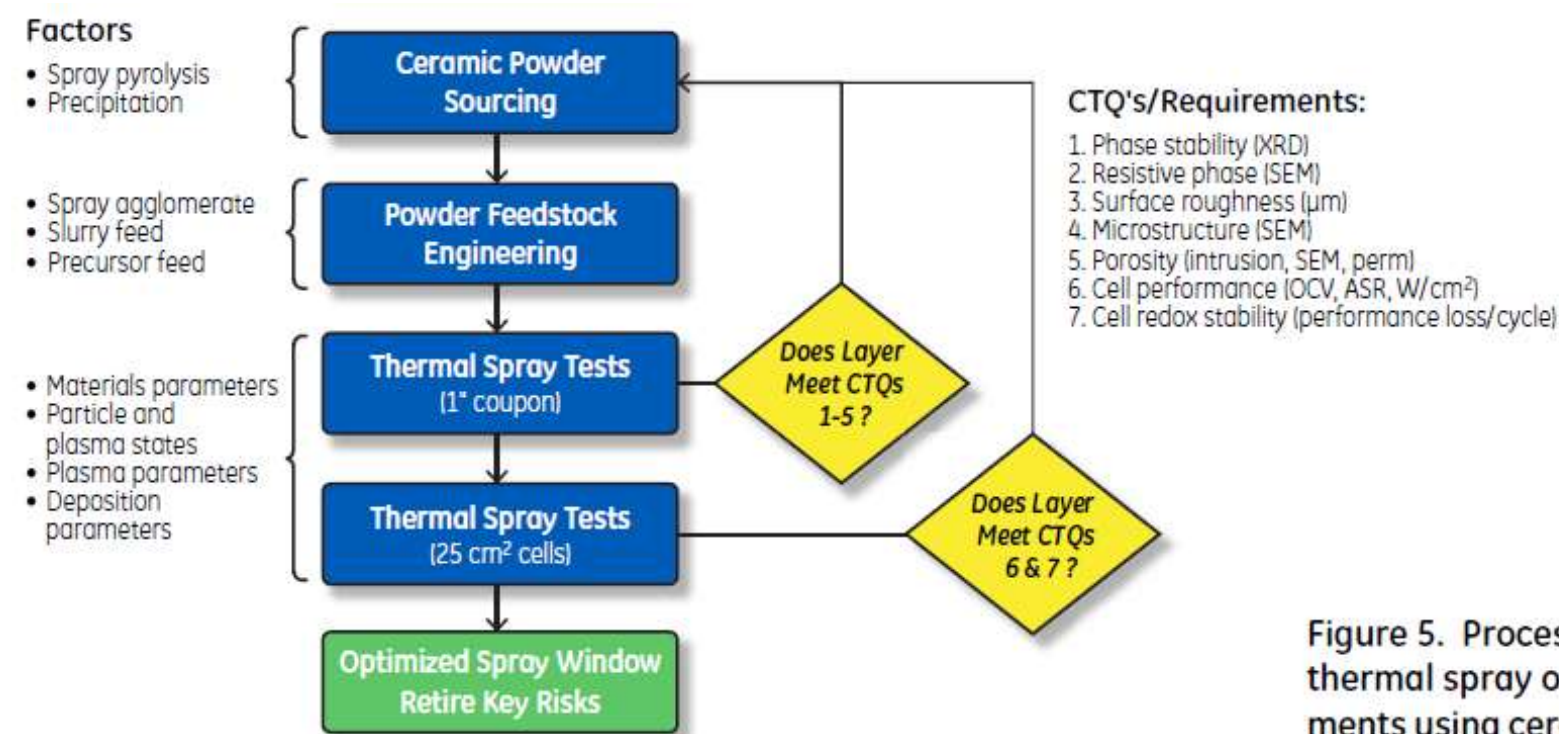
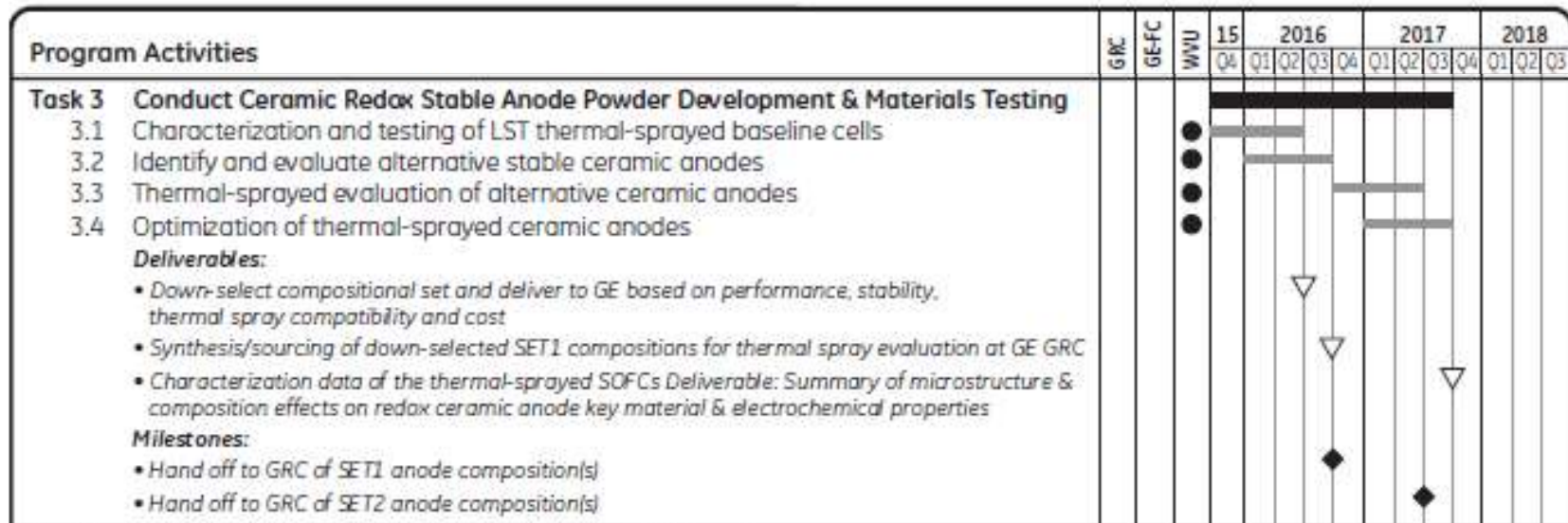


Figure 5. Process flow diagram for thermal spray optimization experiments using ceramic anode materials.



Task 3 – West Virginia University (Year 1 & 2)



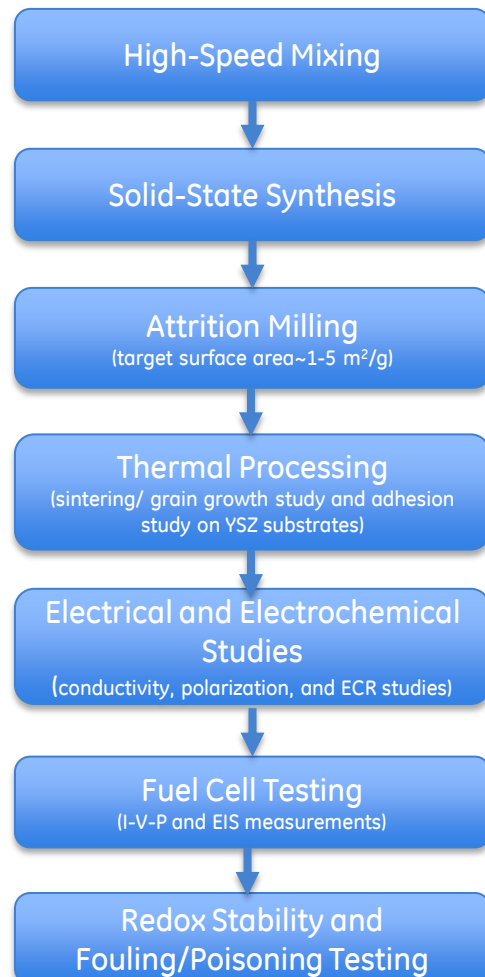
- WVU Students have been selected & admitted (starting Jan 1)
- Leveraging existing WVU group resources to get started on 3.1
- Weekly TCON meetings with GE to keep focused

(Already established operating rhythm, file sharing methods, NDA, Web Conferencing, Shipping methods, began discussions around IP & PR, and started work on Task 3.1)

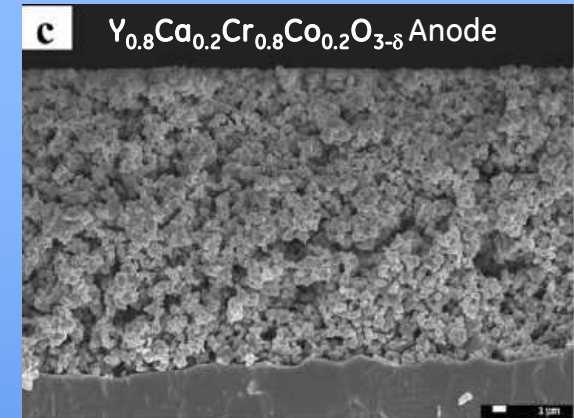
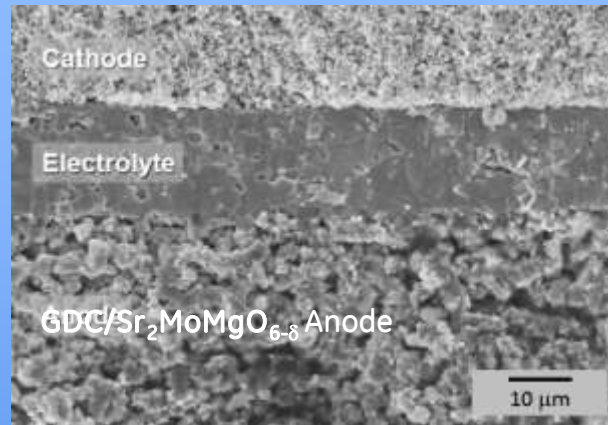
Task 3 goal → “Improve Ceramic Anode Performance”



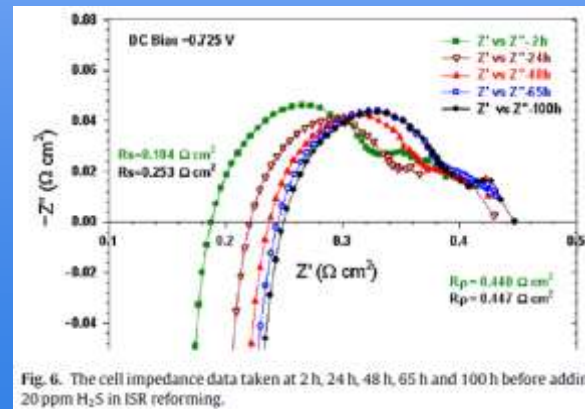
Task 3 – WVU synthesis methods process diagram



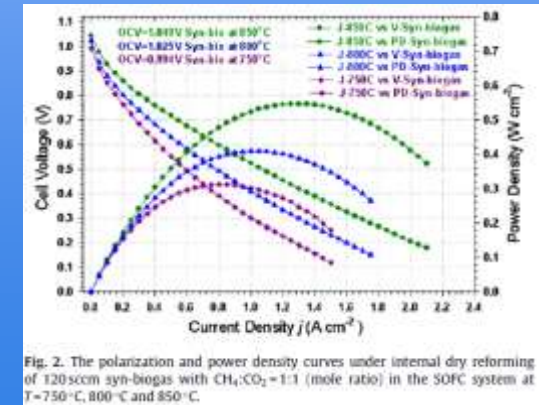
Examples of Anode Research at WVU



Fuel Impurity Testing



Hydrocarbon Fuel Testing



Gansor, P.; Xu, C. C.; Sabolsky, K.; Zondlo, J. W.; Sabolsky, E. M., *Materials Letters* **2013**, 105, 80-83.

Gansor, P.; Xu, C. C.; Sabolsky, K.; Zondlo, J. W.; Sabolsky, E. M., *Journal of Power Sources* **2012**, 198, 7-13.

Chen, G.; Kishimoto, H.; Yamaji, K.; Kuramoto, K.; Gong, M.; Liu, X.; Hackett, G.; Gerdes, K.; Horita, T, *Journal of Electrochemical Society* **2015**, 12, F1342.

Xu, C.; Zondlo, J.W.; Gong, M.; Elizande-Blancas, F.; Liu, X.; Celik, I.B.; *Journal of Power Sources, Journal of Power Sources* **2010**, 195, 4583-4592..



Task 3 – WVU Test Lab

Fuel Cell Testing Capabilities

- Small area (button) SOFC test stands (5 automated SOFC button cell test stands).
- Large area SOFC test stand (30-200 cm² active area) with ability to test in various poisonous gasses (such as H₂S and PH₃).
- Electrical conductivity testing in various gases and fuels (Air, O₂, H₂, N₂, CO, CO₂, H₂O, CH₄) with various impurities (H₂S, PH₃, HCl).
- Electrochemical relaxation (ECR) test stand for quantification of surface reactions.
- 3 Solartron 1260 and 1287 (or equivalent) impedance/gain-phase analyzer with potentiostat systems (for EIS testing).

Fuel Cell Fabrication Capabilities

- 2 Tapecasters and 3 Screenprinters
- Ink jet printer
- Laser cutters
- Laminating presses for large area fuel cells
- Powder mills (roll and attrition mills)
- High-temperature furnaces (air/controlled-atmosphere <1700°C)
- WVU Shared Facilities (all general characterization equipment required, such as SEM, TEM, XRD, XPS, Raman, BET, dilatometry...



Task 4 – GE Global Research (Year 2)

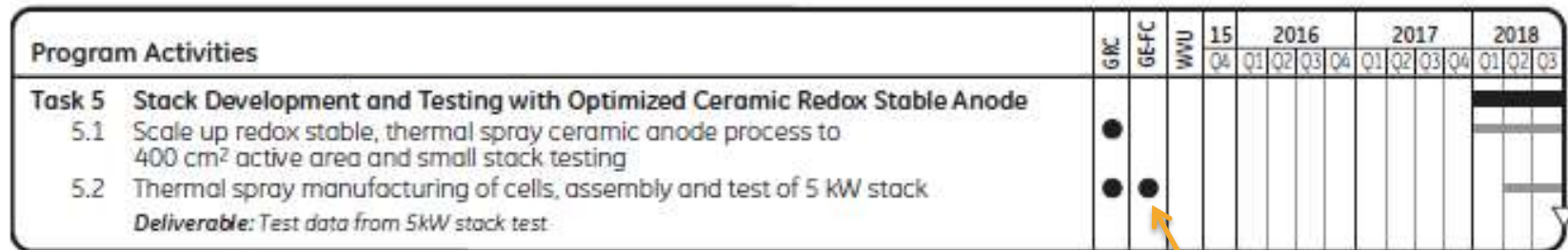
Program Activities		GRC	GEFC	WVU	15	2016				2017				2018		
					04	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
Task 4	Optimize Thermal Spray Ceramic Redox Stable Anodes															
4.1	Develop SET1 and SET2 ceramic redox stable anode thermal spray powders & determine optimal spray conditions for anode deposition	●														
4.2	Evaluate performance and degradation of SET1 and SET2 redox stable anodes on metal supported cell architecture	●														
Deliverables:																
• Summary of SET1 and SET2 optimized thermal spray processing conditions & properties																
• Performance data of SET1 & SET2 ceramic anode redox stable anodes on metal supported cell architecture																
Milestone: Single 100–400cm ² cell, tested for 1000 hr, achieving performance CTQ's.																
Go/No-Go: Does optimized conductive redox stable anode on metal supported cell architecture meet performance CTQ defined in Task 2.1??																

- Combine thermal spray optimization approaches with new higher performing formulations from WVU
- Scale up to larger cell architecture
- Gather data for Go/No Go decision point before Task 5.

Task 4 goal → “Bring it all together”



Task 5 – GE Global Research & GE Fuel Cells (Year 3)



Legend: ◆ Milestone ◇ Decision Point ▽ Deliverable

Figure 2. Schedule for the proposed program.

- Team structure changes (move from R&D -> Demonstration)
- Scale powders, spray large numbers of (400cm²) cells
- Build several smaller practice stacks (using full size cells)
- Assemble and Test a 5kW stack.

Task 5 goal → 5kW Stack Test



Project Milestones and Decision Points

Project Milestones

Task Number	Description	Planned Completion Date	Actual Completion Date
1	Updated Project Management Plan	10/30/2015	10/29/2015
1	Kickoff Meeting	12/31/2015	12/2/2015
2	Demonstration of thermal sprayed LST/CeO ₂ based anode layer	06/31/2016	
2	Demonstration of improved redox performance of ceramic anode based cell	09/30/2016	
3	WVU: Hand off of SET 1 Anode Composition(s) to Global Research	09/30/2016	
3	WVU: Hand off of SET 2 Anode Composition(s) to Global Research	06/31/2017	
4	Single 100-400 cm ² cell, tested for 1000 hr, achieving performance requirements.	12/31/2017	

Decision Points

Task	Go/No-Go Decision Point	Success Criteria
4	Does single 100-400cm ² cell, tested for 1000hr, achieve performance requirements?	Cell test data meets performance requirements to enable SOFC stack development and redox capability?



Acknowledgements

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 - West Virginia University (Dr. Sabolsky, Dr. Liu, Dr. Zondlo)
 - Steven Markovich @ DOE/NETL
-
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